Renewable and Sustainable Energy Reviews 15 (2011) 1258–1270

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Hydrogen rich gas from oil palm biomass as a potential source of renewable energy in Malaysia

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ARTICLE INFO

Article history:
Received 28 June 2010
Accepted 13 October 2010

Keywords:
Hydrogen
Oil palm
Gasification
Thermo-chemical
Energy

ABSTRACT

Oil palm is one of the major economic crops in many countries. Malaysia alone produces about 47% of the world's palm oil supply and can be considered as the world's largest producer and exporter of palm oil. Malaysia also generates huge quantity of oil palm biomass including oil palm trunks, oil palm fronds, empty fruit bunches (EFB), shells and fibers as waste from palm oil fruit harvest and oil extraction processing. At present there is a continuously increasing interest in the utilization of oil palm biomass as a source of clean energy. One of the major interests is hydrogen from oil palm biomass. Hydrogen from biomass is a clean and efficient energy source and is expected to take a significant role in future energy demand due to the raw material availability.

This paper presents a review which focuses on different types of thermo-chemical processes for conversion of oil palm biomass to hydrogen rich gas. This paper offers a concise and up-to-date scenario of the present status of oil palm industry in contributing towards sustainable and renewable energy.

Contents

Abbreviations: 8MP, Eight Malaysian Plans; Al, aluminum; Al_2O_3, aluminum oxide; BioGen, Biomass-based Power Generation and Cogeneration in the Malaysian Palm Oil Industry; $Ca(OH)_2$, calcium hydroxide; $CaCO_3$, calcium carbonate; CaO, calcium oxide; Ce, cerium; CeO_2, cesium oxide; CH_4, methane; Co, carbon monoxide; CO_2, carbon dioxide; Cr_2O_3, chrome oxide; $CsCO_3$, cesium carbonate; Cu, copper; EFB, empty fruit bunches; Fe, iron; Fe_2O_3, iron oxide; FELDA, Federal Land Development Authority; FFB, fresh fruit bunch; GHG, greenhouse gases; H_2, hydrogen; K_2CO_3, potassium carbonate; KCl, potassium chloride; $KHCO_3$, potassium bicarbonate; KOH, potassium hydroxide; La, lanthanum; MF, mesocarp fiber; MnT, million tonnes; Mtoe, million tonnes of oil equivalents; MW, Mega Watt; Na_2CO_3, sodium carbonate; NaCl, sodium chloride; Ni, nickel; NiO, nickel oxide; NO_x, nitrogen oxides; OPP3, Third Outline Perspective Plan; PAH, polyaromatic hydrocarbon; Pd, palladium; POME, palm oil mill effluent; Pt, platinum; Rh, rhodium; Ru, ruthenium; $RuCl_3$, ruthenium chloride; SCORE, Special Committee on Renewable Energy; SCW, supercritical water; SiO_2, silicon dioxide; SO_2, sulfur oxide; SREP, Small Renewable Energy Program; TiO_2, titanium oxide; TNB, Tenaga National Berhad; UNDP, United Nations Development Programme; UNFCCC, United Nations Framework Convention on Climate Change; $ZnCl_2$, zinc chloride; Zr, zirconium.

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doi:10.1016/j.rser.2010.10.003

1. Introduction

The world's energy consumption, especially in the transportation sector is still dependent on fossil fuels [1]. This leads to serious energy crisis and environmental problems, i.e. fossil fuel depletion and pollutant emission. The increasing energy demands will speed up the exhaustion of the finite fossil fuel. Moreover combustion of fossil fuel produces substantial greenhouse gases (GHG) and toxic gases such as CO_2, CH_4, SO_2, NO_x and other pollutants, causing global warming and acid rain [2].

Progressive emission of GHG has been identified as the main cause of global warming and the target is to limit global temperature rise to a maximum 2 °C [3]. Since the closing of the United Nations Climate Change Conference in Copenhagen, the United Nations Framework Convention on Climate Change (UNFCCC) has received submissions of national pledges to cut or limit emissions of greenhouse gases by 2020 from 75 Parties, which together account for more than 80% of global emissions from energy use. To achieve this, it is important to develop suitable long-term strategies based on utilization of renewable fuel that would gradually substitute the declining fossil fuel production; the alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available [4].

Biomass is one of the most abundant renewable resources; it is formed by fixing carbon dioxide in the atmosphere during the process of plant photosynthesis and, therefore, it is carbon neutral in its lifecycle. Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security.

At present the palm oil industry generates large volume of biomass from the oil extraction process such as mesocarp fiber, shell, empty fruit bunch (EFB) and palm oil effluent (POME). The world annual production of oil palm residues amounts to 184 million tonnes. About 53 million tonnes of residues are produced from oil palm trees every year in Malaysia alone, and it is increasing annually by 5% [5].

Biofuels are liquid or gaseous fuels for power plants and transport sectors that are produced from renewable sources such as biomass [6]. Hydrogen has been found to be well suited for this purpose as it is clean and a high calorific value fuel.

From the above perspective, worldwide research is focusing towards the hydrogen economy. Hydrogen is expected to become one of the major sources of energy in the future. As the Malaysian palm oil industry produces huge quantities of oil palm residues every year, there has been greater interest in the utilization of oil palm biomass for production of biofuels.

This review is focused on the thermo-chemical conversion routes for hydrogen production based on oil palm biomass because it is more economical and practical if the hydrogen is to be used as energy. Presently, hydrogen production from other methods such as natural gas reforming is for the purpose of petrochemical production but it is not economical for energy. A brief introduction on oil palm biomass in Malaysia is presented followed by a review of the effect of various types of catalyst on hydrogen yield from biomass.

2. Availability of oil palm biomass in Malaysia

The oil palm (*Elaeis guineensis*) originates from South Africa. It grows well in all tropical areas of the world and it has become one of the main industrial crops. It was first introduced to Malaysia in 1870 as an ornamental plant. Mature trees are single-stemmed, and grow up to 20 m tall. The fruit grows in large bunches; each bunch can have up to 200 individual fruits and weigh up to 10–30 kg. It takes 5–6 months from pollination to maturity. The fruit comprises an oily, fleshy outer layer (the pericarp), with a single seed (kernel), which is also rich in oil [7]. Oil palms fruit is usually harvested after 3 years from planting, but maximum yield can be achieved in the 12–14th year, and then continuously declines until the end of the 25th year [8]. Pictures 1–4 show the palm tree and its accessories. The palm oil tree is shown in Picture 1, whereas Pictures 2–4 show the palm oil fruit, fresh fruit bunch (FFB) and empty fruit bunch (EFB), respectively.



Picture 1. Palm oil tree.

The Malaysian palm oil industry has grown tremendously over the last 25 years to become a very important agriculture-based industry, where the country is today the world's leading producer and exporter of palm oil. This can be clearly seen in Fig. 1. The palm oil production has increased from 2.5 million tonnes in 1980 to 17.8 million tonnes in 2009 [9] and presently Malaysia's produc-



Picture 2. Palm oil fruit.



Picture 3. Fresh fruit bunches (FFB).



Picture 4. Empty fruit bunch (EFB).

tion accounts for about 47% of the world palm oil production. Fig. 2 shows the trend of palm oil production in Malaysia between the years 2004 and 2009 in million tonnes (MnT).

Oil palm is a multipurpose plantation and also a prolific producer of biomass as raw materials for many value-added industries. Palm oil forms about 10% of the whole palm oil tree, while the other 90% remains biomass [10]. For example, fresh fruit bunch contains only 21% palm oil, while the rest 14–15% fiber, 6–7% palm kernel, 6–7% shell and 23% empty fruit bunch (EFB) are left as biomass [11].

Currently, the Malaysian palm oil industry generates huge quantities of oil palm biomass including oil palm trunks, oil palm fronds, empty fruit bunches (EFB), shells and fibers. Fig. 3 shows the types of biomass produced from oil palm tree and the quantities pro-

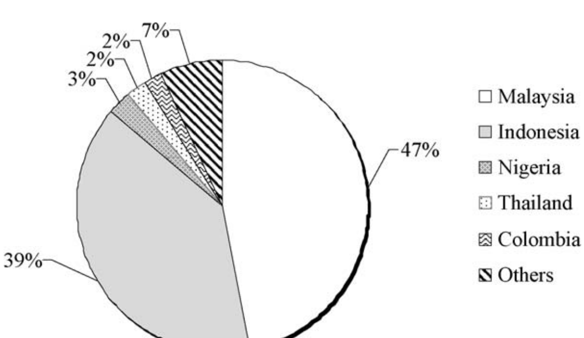


Fig. 1. World palm oil production in the year 2009.

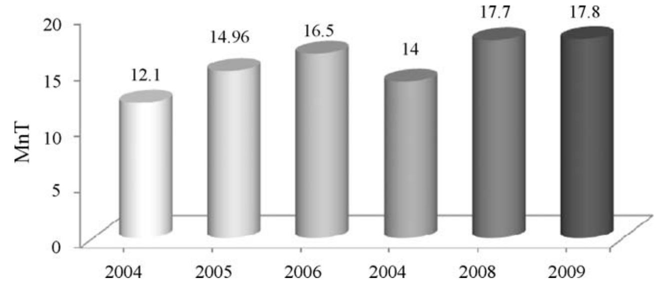


Fig. 2. Palm oil production in Malaysia from 2004 to 2009.

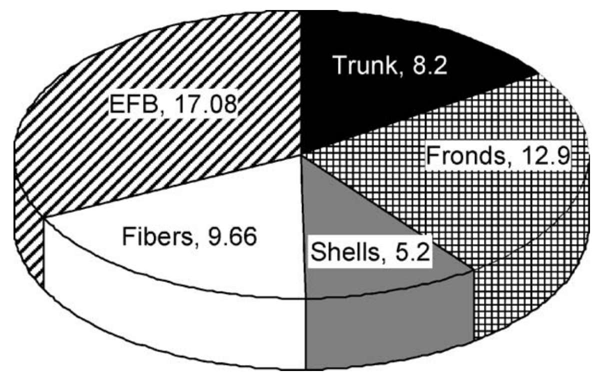


Fig. 3. Types of oil palm biomass produce in Malaysia in 2009 in MnT/year.

duced per annum in million tonnes. This oil palm biomass has a high potential to be converted into renewable energy.

Oil palm fronds are available daily throughout the year when the palms are pruned during the harvesting of fresh fruit bunches. The fronds are left rotting on the palm oil trees, mainly for soil conversion, erosion control and ultimately the long-term benefit of nutrient recycling [12]. Oil palm trunk is obtained during the replantation of the oil palm trees. EFB, mesocarp fiber (MF) and shells are collected during the pressing of sterilized fruits [13].

The chemical and physical properties of oil palm biomass vary according to their diverse origins and plant species. Generally cellulose, hemicelluloses, lignin and ash are the major oil palm biomass components [14,15]. Table 1 tabulates the chemical composition of oil palm biomass.

Cellulose is a high molecular weight linear polymer of β-(1 → 4)-D-glucopyranose units in the $^4C_1$ conformation, whereas hemicellulose is a complex mixture of various polymerized monosaccharide such as glucose, mannose, galactose, xylose, arabinose, methylglucoronic and galaturonic acids. On the other hand, lignin, found in the cell wall, is a polymeric aromatic polymer and it is a three-dimensional, highly branched, polyphenolic substance that consist of an irregular array of variously bonded "hydroxyl-" and "methoxyl-" substituted phenylpropane units. Fig. 4 portrays the textural structure of biomass, whereas Figs. 5–7 illustrate the chemical structure of cellulose, hemicellulose and lignin, respectively.

Table 1
Chemical composition of oil palm biomass.

Component	Oil palm biomass chemical composition (wt.%)				
	EFB	Shell	Frond	Fiber	Trunk
Reference	[16]	[17]	[18]	[19]	[20]
Cellulose	38.3	20.8	49.8	34.5	37.14
Hemicellulose	35.3	22.7	83.5	31.8	31.8
Lignin	22.1	50.7	20.5	25.7	22.3
Ash	1.6	1.0	2.4	3.5	4.3

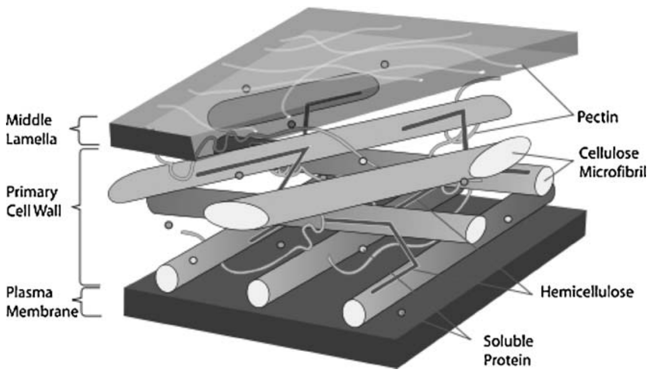


Fig. 4. Texture structure of biomass [21].

3. Biofuel and biopower programs in Malaysia

Malaysia is blessed with natural resources, particularly crude oil and natural gas, which are the main sources of energy. However, due to increasing demand of energy sources and depleting supply of natural sources, the Malaysian government has to embark on alternative energy sources. Rising crude oil prices have led to higher government expenditures on subsidies to keep retail fuel price at relative low levels. Consequently, biofuel as an alternative energy source has become more viable. The government has identified oil palm biomass as the biggest resource that can be easily developed, thus having the greatest potential for bringing renewable energy into the mainstream energy supply [22]. Oil palm biomass can be used to make the same products that are created by fossil fuels like syngas, diesel, ethanol, etc.

In order to meet the increasing demand of energy in Malaysia and to deal with an unstable palm oil price and fast depletion of fossil fuels, the Malaysian government formulated the National biofuel program in ensuring sustainable development of the energy sector as well as promoting a cleaner environment. As illustrated in Fig. 8, according to the rapid increase in energy demand in Malaysia, it is expected to reach 100 Mtoe (million tonnes of oil equivalent) in 2030 compared to 50 Mtoe in 2010 [23]. Owing to this, the government has targeted the renewable energy as the fifth fuel after oil, gas, hydro and coal, initiated earlier under the Third Outline Perspective Plan (OPP3) period (2001–2010) [24] and Eight Malaysian Plan (8MP) period (2001–2005) [25].

At present, there are a number of Small Renewable Energy Program (SREP) projects utilizing oil palm biomass in Malaysia. In 2004, 65 SREP projects had been approved. Out of these projects, only 27 projects used oil palm biomass as fuel source providing 214.7 MW capacity [26]. At the end of 2005, only 12 MW of electricity from renewable energy sources was connected to the national grid [27]. Table 2 represents the status of SREP projects approved by special committee on renewable energy (SCORE) in 2004.

Japanese company “Chubu Electric Power” announced in 2006, plans to build two biomass power plants in the eastern part of Sabah, Malaysia. These biomass plants will use EFB as renewable energy source to generate a 10 MW small-scale electric power plant [28]. The first power plant has already begun operation in the first quarter of 2008 [29].

Another biomass power plant project had been proposed in Pantai Remis, Perak, Malaysia by Bumobipower Sdn. Shd. The project is to generate electricity utilizing EFB as fuel, and to develop an enhanced approach to waste-disposal in the palm oil industry. This project aims to generate 11.5 MW capacity [30].

In March 2008, Tenaga National Berhad (TNB), the largest power company in Malaysia signed an agreement with Federal Land Development Authority (FELDA) and Japan’s J-Power to develop a biomass power plant in Jengka, Pahang. This project uses EFB as fuel source to generate electricity and is expected to be completed by the end of 2010. The generation capacity of this plant is 10 MW and would be connected to the grid [23].

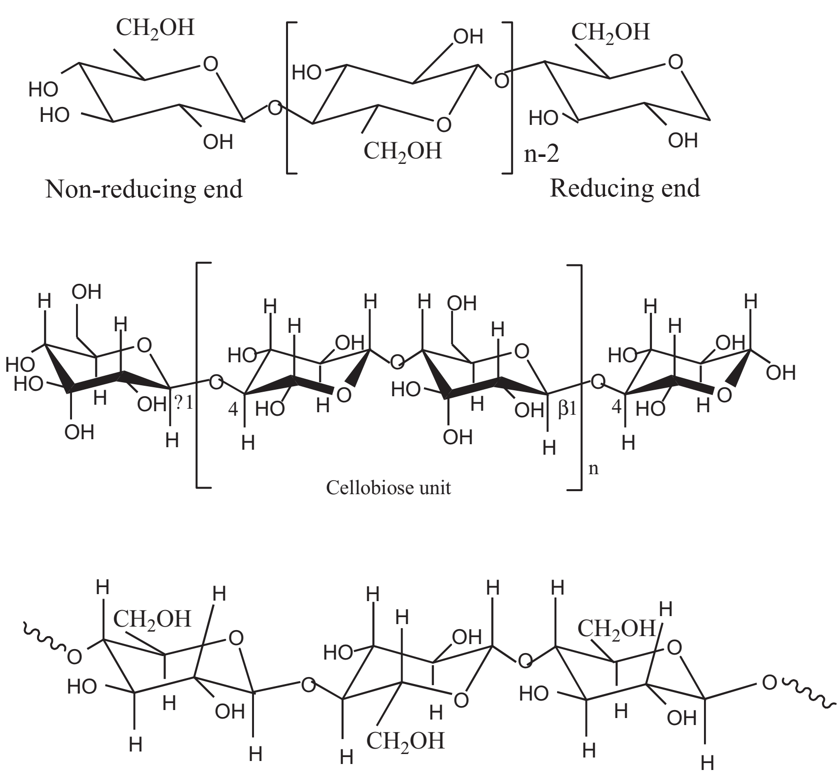


Fig. 5. Chemical structure of cellulose.

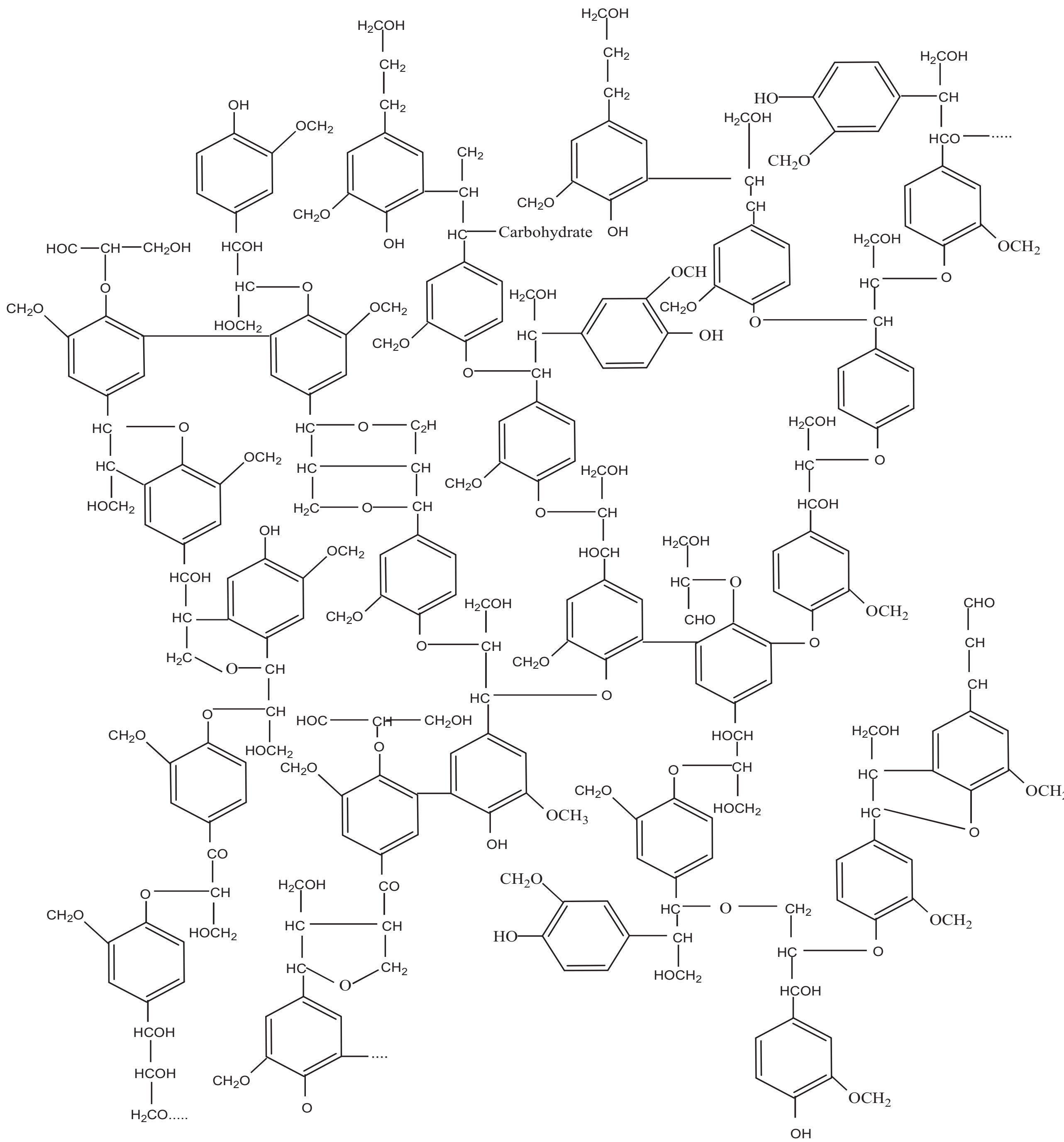


Fig. 6. Chemical structure of main components of hemicelluloses.

Table 2
Status of SREP projects approved by SCORE in 2004 [26].

No.	Type	Energy source	Approved application	Grid connected capacity	%
1	Biomass	Oil palm biomass	27	214.7	58.2
		Wood residues	1	6.6	1.7
		Rice husks	2	12	3.25
		Municipal solid waste	1	5	1.35
		Mixed fuel	3	19.2	5.2
2	Landfill gas		5	10.2	2.76
3	Mini-hydro		26	101.6	27.54
Total			65	368.9	100

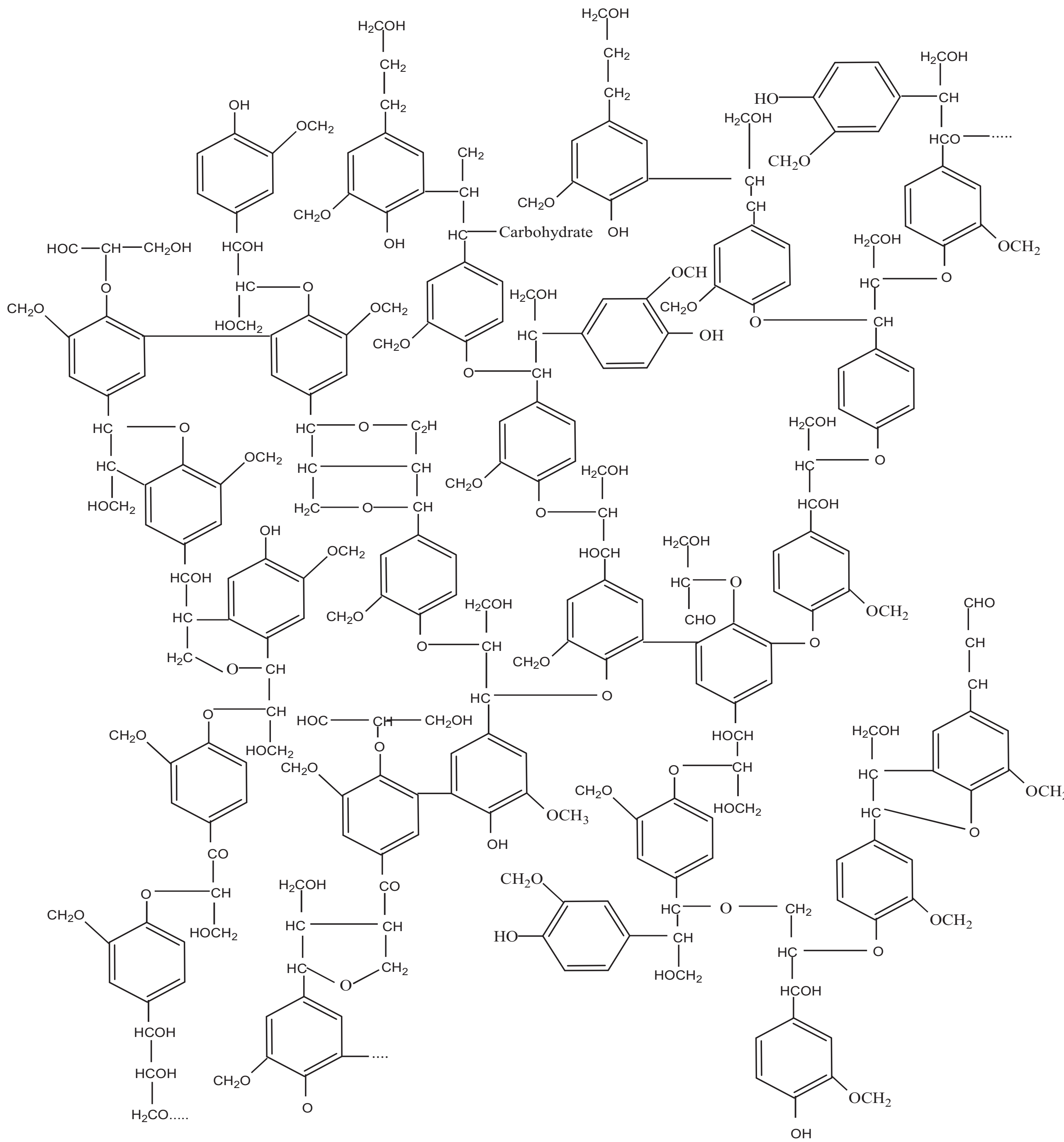


Fig. 7. Chemical structure of lignin.

In 2002, the United Nations Development Programme (UNDP) and Malaysian government implemented the national project called Biomass-based Power Generation and Cogeneration in the Malaysian Palm Oil Industry (BioGen). The main objectives are to promote the use of biomass wastes from the palm oil industry in Malaysia for power generation, resulting in the long-term reduction of the growth rate of GHG emissions. The strategy of BioGen project involves implementation of biomass-based grid connected power generation and combined heat and power in Malaysia. This project faced many inter-related and complex problems that have led to the delays and unfortunately did not achieve the desired results.

It is rather surprising that even in a country like Malaysia where biomass can be easily obtained; the use of renewable energy is still low. Therefore, further efforts, researches and strategic plans must be developed and implemented correctly.

At present, there is a greater interest in the utilization of the oil palm biomass for the production of environmental friendly biofuels and this could make Malaysia to be one of the major contributors of renewable energy in the world. Fig. 9 shows the Malaysian roadmap for productions of hydrogen from biomass until 2030.

4. Hydrogen

Hydrogen gas was first artificially produced in the early 16th century, via mixing of metals like zinc with dilute acids. Henry Cavendish in 1766 was first to recognize the gas. He called this gas

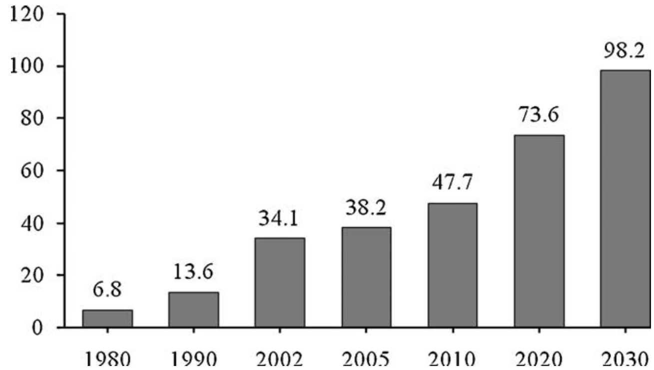


Fig. 8. Energy demand in Malaysia [23].

as inflammable air since it burned when ignited. Later, Lavoisier found that the gas would produce water when burned, a property which later gave it its name as "Hydrogen" (Greek: Hydru = water forming). At standard temperature and pressure, hydrogen is a colorless, odorless, nonmetallic, tasteless and highly combustible diatomic gas with molecular formula H_2. Various physical properties of hydrogen are listed in Table 3 [31].

Hydrogen can be produced using diverse, domestic resources including fossil fuels, natural gas, nuclear and biomass and other renewable energy technologies such as wind, solar, geothermal and hydroelectric power.

Presently, worldwide research is focusing towards the hydrogen production from biomass, since it is expected to become a major source of energy and plays an important role in economic development.

4.1. Hydrogen applications

Hydrogen can be used for various applications covering many industries, including [32,33]:

- Petroleum and chemical industries, like fossil fuels processing, ammonia manufacturing and petrochemicals (hydrodealkylation, hydrodesulfurization and hydrocracking).
- Hydrogenation agent to increase the level of saturation of unsaturated fats and oil.
- Metal production and fabrication.
- Shielding gas in welding methods such as atomic hydrogen welding.
- Rotor coolant in electrical generators at power stations.
- Production of float glass.
- Filling gas in balloons and airships.
- Energy storage technology.
- Electronic industry.
- Production and processing of silicon.
- Pharmaceuticals.
- Fuel for rocket propulsion.
- Power generation with fuel cells.
- Transportation sector.

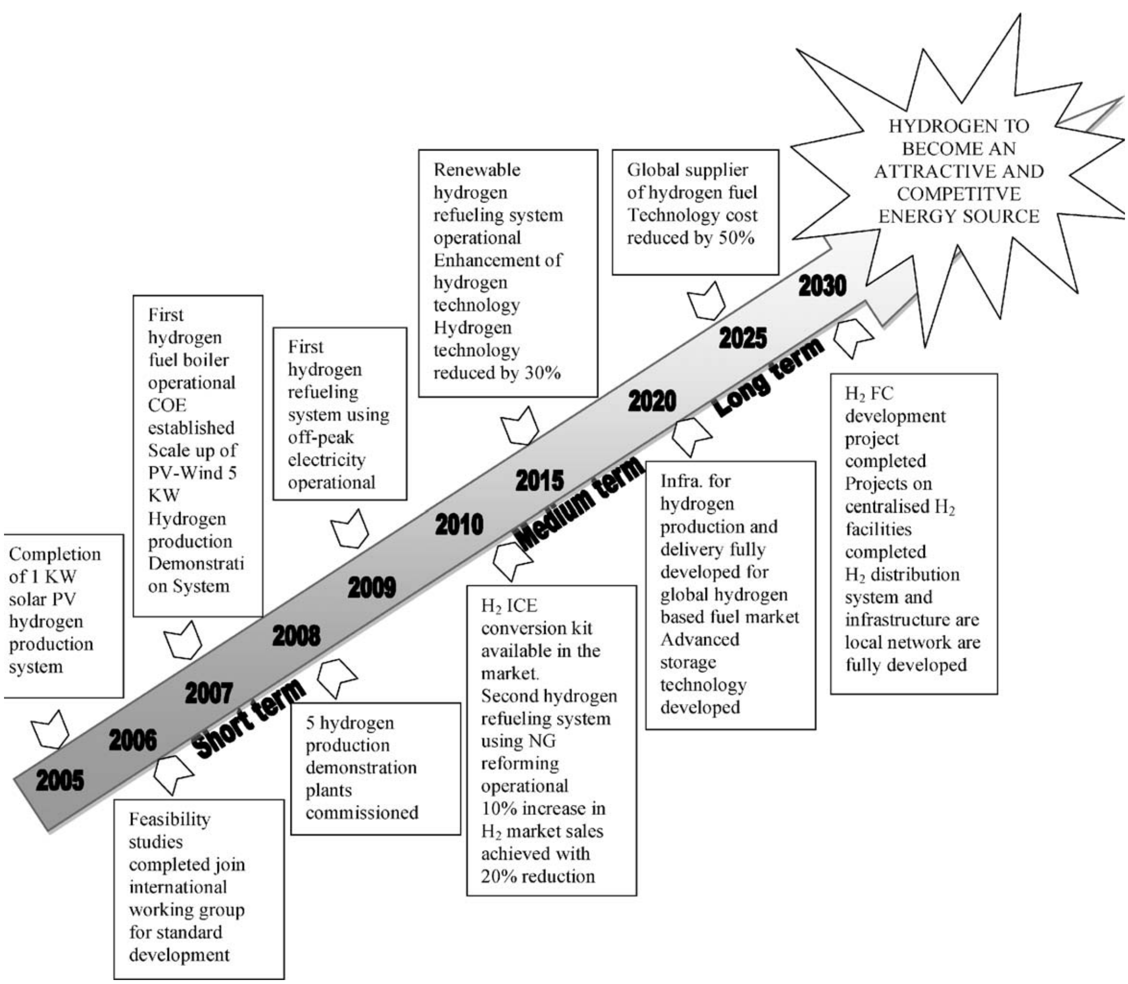


Fig. 9. Hydrogen roadmap for Malaysia [26].

Table 3
Physical properties of hydrogen [31].

Liquid phase	
Density (kg/m^3)	70.96
Enthalpy (J mol)	548.3
Entropy (J/mol/K)	34.92
C_p (J/mol/K)	19.7
C_v (J/mol/K)	11.6
Viscosity (mPa s)	13.3×10^{-3}
Thermal conductivity (W/m/K)	100×10^{-3}
Compressibility factor	0.01698
Gaseous phase	
Density (kg/m^3)	1.331
Enthalpy (J mol)	1447.4
Entropy (J/mol/K)	78.94
C_p (J/mol/K)	24.60
C_v (J/mol/K)	13.20
Viscosity (mPa s)	1.11×10^{-3}
Thermal conductivity (W/m/K)	16.5×10^{-3}
Compressibility factor	0.906
Critical point at STP	
Density (kg/m^3)	0.0899
C_p (J/mol/K)	28.59
C_v (J/mol/K)	20.3
Viscosity (m Pa s)	8.34×10^{-3}
Thermal conductivity (W/m/K)	173.9×10^{-3}
Compressibility factor	1.00042
Combustion and explosion	
Density (kg/m^3) at STP	0.084
Heat of vaporization (J/g)	445.6
High heating value (kJ/g)	141.8
Lower heating value (kJ/g)	119.93
Diffusion coefficient in air at STP (cm^2 s)	0.61
Thermal conductivity in air at STP (W/m/K)	1.897
Detonability limits in air (vol.%)	18.3–59
Flammability limits in air (vol.%)	4.0–75
Limiting oxygen index (vol.%)	5.0
Minimum energy of ignition in air (MJ)	0.02
Auto ignition temperature (K)	858
Flame temperature in air (K)	2318
Energy of explosion mass related g TNT (g)	24.0
Energy of explosion volume related g TNT (m^3)	2.02

5. Energy production processes from biomass

The main routes for biomass conversion into energy are bio-chemical/biological processes and thermo-chemical processes. The first routes are attractive due to lower secondary pollution generated from microorganism conversion method; however, major drawbacks from these processes are difficult to culture microorganism, low hydrogen generation efficiency and higher operating temperature needed to operate. Fig. 10 demonstrates the energy production technologies based on biomass.

On the other hand, thermo-chemical conversion routes encompass four different processes as described below [31,32,34]:

5.1. Combustion

The direct burning of biomass in air to convert the chemical energy stored in biomass into heat, mechanical power or electricity using equipment such as stoves, furnaces, boilers or steam turbines. Combustion of biomass produces hot gases in the temperature range of 700–1000 °C. Combustion is feasible for biomass having less than 50% moisture content, otherwise the biomass have to be pre-dried [35]. As the energy efficiency is low (10–30%) and the pollutant emissions are the by-products, combustion is not a suitable hydrogen production for sustainable development.

5.2. Liquefaction

Thermo-chemical liquefaction is one of the methods to convert biomass to fluid fuel. In this process, biomass is heated to 250–350 °C in water at a pressure of 5–20 MPa in the absence of air. Solvent or catalyst can be added in the process [36]. The disadvantages of biomass liquefaction are that it is very difficult to achieve the operating condition and its production of hydrogen is low. Therefore, liquefaction is not favorable for hydrogen production.

5.3. Pyrolysis

Pyrolysis is a conversion of biomass to liquid, solid and gas mixture by direct thermal decomposition of the biomass in the absence

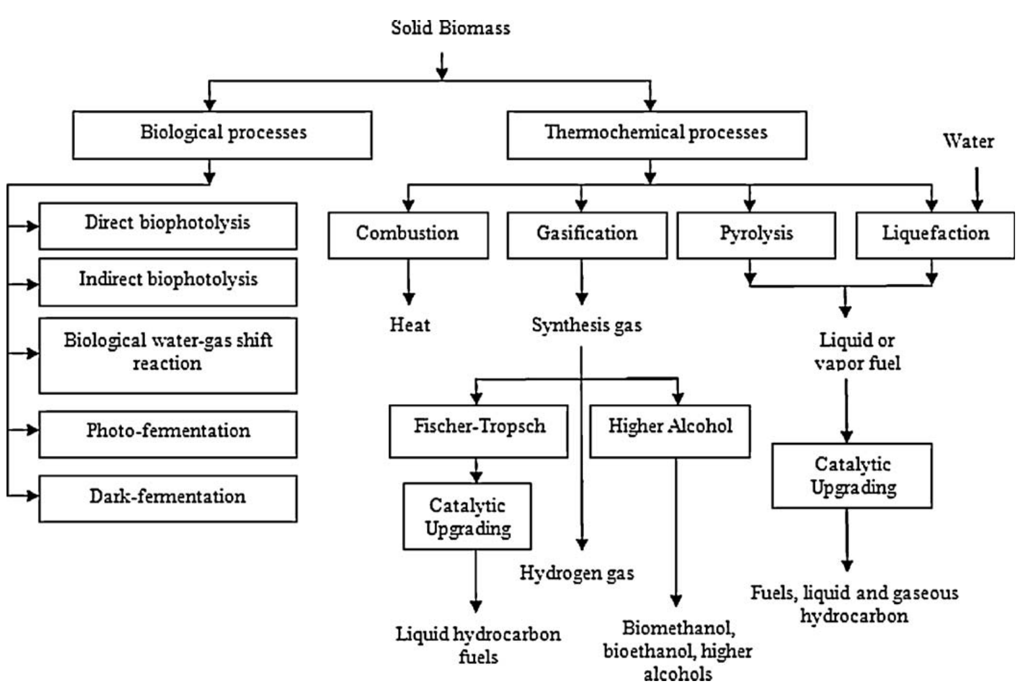


Fig. 10. Energy production processes based on biomass.

of oxygen at temperature range of 350–550 °C [37]. The pyrolysis processes under development are based on two different concepts namely slow pyrolysis and fast or flash pyrolysis. These differ from each other in terms of chemistry, yields and quality of products. Liquids produced from pyrolysis are called bio-oil; it is a complex mixture of aliphatic and aromatic compounds [38]. Pyrolysis reaction is an endothermic reaction as shown below:

$$\text{biomass} + \text{heat} \rightarrow \text{bio-oil} + \text{gas} + \text{char} \quad (1)$$

5.4. Gasification

Unlike pyrolysis, gasification is the conversion of biomass into combustible gas mixture at high temperature range of 700–1000 °C, with a controlled amount of oxygen and/or steam (partial oxidation). The resulting gas mixture is called synthesis gas or syngas. This conversion process is expressed as [34]:

$$\text{biomass} + \text{heat} \rightarrow H_2 + CO + CO_2 + CH_4 + \text{hydrocarbon} + \text{char} \quad (2)$$

The oxidant agent can be air, hydrogen, steam, CO_2 or their mixtures. Air is a cheap and widely used as a gasifying agent, containing a large amount of nitrogen, which reduces the heating value of the syngas produced [39]. Usage of oxygen as a gasifying agent could produce a better quality syngas of medium heating value, but it requires a pure oxygen supply which leads to simultaneous problem of cost and safety [34]. The use of CO_2 as the gasifying agent is promising because of its presence in the syngas. CO_2 with a nickel-based catalyst can convert char, tar and CH_4 into H_2 and/or CO, thus leading to higher amount of H_2 and CO contents in the syngas produced [40]. If steam is used as the gasifying agent, the heating value and H_2 content in the syngas can be increased, however, the operational costs will also be increased due to the demand for an external heat source for steam production [41].

During the gasification process a number of exothermic and endothermic reactions take place. Heating and drying are endothermic processes, requiring a source of heat to drive them. This heat can be supplied by an external source in a process called indirectly heated gasification. More typically, a small amount of air or oxygen is admitted for the purpose of partial oxidation, which releases sufficient heat for drying and pyrolysis as well as for the subsequent endothermic chemical reactions. During gasification, physical, chemical and thermal processes may take place sequentially or simultaneously, depending on the reactor design and the feedstock.

Gasification is a solid-gas reaction converting solid carbon into gaseous CO, CO_2, H_2 and CH_4. Gasification reactions can be represented by [42]:

$$\text{combustionreaction}: \quad C + 1/2O_2 \rightarrow CO \quad (3)$$

$$CO + 1/2O_2 \rightarrow CO_2 \quad (4)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad (5)$$

$$\text{Boudouardreaction}: \quad C + CO_2 \leftrightarrow 2CO \quad (6)$$

$$\text{watergasreaction}: \quad C + H_2O \leftrightarrow CO + H_2 \quad (7)$$

$$\text{methanationreaction}: \quad C + 2H_2 \leftrightarrow CH_4 \quad (8)$$

$$\text{water-gasshiftreaction}: \quad CO + H_2O \leftrightarrow H_2 + CO_2 \quad (9)$$

$$\text{steammethanereformingreaction}: \quad CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (10)$$

6. Technologies for hydrogen production from biomass

6.1. Hydrogen production from gasification in supercritical water (SCW)

In this process, biomass is treated in supercritical water to be converted into fuel gases, which are rich in hydrogen. Water plays various roles in facilitating the gasification reaction, due to its unique ability and properties. The properties of water displayed beyond critical point plays significant role for chemical reactions. The hot compressed water molecules can participate in various elementary reaction steps as reactant, catalyst as well as medium. The overall reaction can be written as [43]:

$$2C_6H_{12}O_6 + 7H_2O \rightarrow 15H_2 + 9CO_2 + CO + 2CH_4 \quad (11)$$

At temperature about 600 °C in supercritical water, a hydrogen-rich gas can be formed from different types of biomass with almost complete conversion of the biomass into gases. Most experimental studies have found that reaction temperatures (500–700 °C) will have a strong effect on yields and gas compositions, whereas pressure (above the critical) has little effect on the extent of gasification or the composition. Studies have been conducted with and without catalysts and the common catalysts include activated carbon and alkali salts [44].

Several research groups studied the gasification of different biomass in supercritical water using different types of catalysts. A summary of hydrogen production via gasification in supercritical water researches with different operating conditions and reactors is tabulated in Table 4.

6.2. Hydrogen from pyrolysis

Although most pyrolysis processes are designed for bio-oil production, hydrogen can be produced through fast pyrolysis at high temperature and long gas residence time. In order to evaluate hydrogen production from biomass pyrolysis, extensive experimental investigations have been conducted. Agricultural residues, organic wastes, mixed biomass and synthetic polymers have been widely used for hydrogen production [34]. Fast pyrolysis processes produce 60–75 wt.% of bio-oil, 15–25 wt.% of solid char and 10–20% of gases, depending on the feedstock used [53]. With the aid of catalysts incorporated in the pyrolysis process, the quantity and quality of the gas product can be improved. Different types of catalysts were used to accelerate process reaction rate such as inorganic salts (chlorides and carbonates) [34,54], metal oxides [55,56] and nickel-based catalyst [55]. Catalyst can be placed inside the pyrolysis reactor in the layer of glass wool or it can be dry mixed with feedstock biomass.

Table 5 presents the pyrolysis of different biomass for production of hydrogen using different catalysts.

6.3. Hydrogen from gasification

Gasification is an important process for recovering energy from biomass. During gasification process, biomass is thermally decomposed to small quantities of char, liquid oil and high production of gaseous products under limited presence of oxygen. The product yields and the composition of gases are dependent on several parameters including temperature, gasifying agent, biomass species, particle size, heating rate, operating pressure, equivalence ratio, catalyst addition and reactor configuration.

Biomass gasification in producing a hydrogen rich product has attracted great attentions in recent years. Apparently, the way to force the biomass gasification process into shift towards the maximum hydrogen rich end product is becoming a priority topic.

Table 4
The gasification in supercritical water of different biomass for the production of hydrogen using different types of catalysts.

Biomass	Catalyst	Reactor type	Temperature (°C)	Pressure (MPa)	Hydrogen yield	References
Glucose	$Ni/\gamma Al_2O_3$ $Ni/CeO_2-\gamma Al_2O_3$	Autoclave	400	24.5	12.7 mol H_2/kg feed	[45]
Glucose	R-nickel	Batch microreactor	340–380	15–25	6 mmol H_2/g feed	[46,47]
Glucose	Ni/activated charcoal	Packed bed	575–725	28	2.45 mol H_2/mol feed	[48]
Lignin	$RuCl_3/TiO_2$	Tubular	400	37.1	–	[49]
Paper sludge Black liquor	Alkali salts	Tubular	500–650	25	24 mol H_2/kg feed	[50]
Cellulose	K_2CO_3 $Ca(OH)_2$	High pressure autoclave	450–500	24–26	8.2 mol H_2/kg feed	[51]
Cellulose sawdust	CeO_2, Ru/C $(CeZr)xO_2$	Tubular	500	27	4 g H_2/100 g feed	[52]

The use of some additives like dolomite, olivine, alkaline metal oxide and nickel-based inside the gasifier could help improving gas product quality, conversion efficiency and tar reduction. In order to prevent the formation of ash in gasification process that may cause deposition, sintering, fouling, slugging and agglomeration problems, fractionation and leaching have been employed [60,61]. The addition of salts such as KOH, K_2CO_3 and $KHCO_3$ cause an increase in H_2 and a decrease in CO yield by acceleration of the water-gas shift reaction [62]. However, it should be noted that alkali salts in biomass can cause plugging and deactivation of other metal catalysts [63].

Several research groups studied the gasification of biomass under different conditions using different types of catalyst to get the maximum hydrogen yield with different types of reactor. The catalysts used in biomass conversion could be divided into two groups which depend on the position of the catalyst in the gasification process. The first group is known as primary catalysts, where the catalysts are dry mixed with biomass feedstock or by wet impregnation, while the second group of catalysts is secondary catalyst, where the catalysts are placed on downstream from the gasifier. Dolomite and CeO_2/SiO_2 supported Ni, Pt, Pd, Ru and alkaline metal oxides can catalyze the gasification process to reduce tar formation and improve gas production quality and conversion efficiency [64–66]. Although $Rh/CeO_2/SiO_2$ has been reported to be the most effective catalyst reducing tar formation [66], nickel-based catalysts are highly active for tar reduction.

A summary of gasification biomass research using primary catalysts is shown in Table 6.

7. Hot gas cleaning technologies

The presence of condensable organic compounds and methane in the product gas produced from biomass gasification process renders this gas unsuitable for specific application. Elimination of the tar and methane by a suitable cheap technology will enhance the economic viability of biomass gasification. The continual build-up of tar present in the product gas can cause blockage and corrosion, and reduce overall efficiency of gas yield. The presence of impurities such as methane can also affect the end usage of the syngas.

Many mechanical methods such as cyclones, baffle filter, bag filter, ceramic filter, candle filter, separators and scrubbers have been used to remove dust and tar from syngas after gasification [80]. Most of these mechanical methods for gas cleaning operate only at low temperature (<200 °C). Hot gas cleaning could improve energy efficiency and reduce operating costs for syngas utilization [81]. Tar removal is a key issue for a successful application of biomass-derived syngas.

8. Catalytic cracking of tar

Tar is a complex mixture of condensable hydrocarbons, which includes single ring to 5-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polyaromatic hydrocarbon (PAH) [82]. In the past three decades, interest has grown on the subject of catalysis for biomass gasification. The advances in this area have been driven by the need to produce a tar-free product gas from the gasification of biomass, since the removal of tars and the reduction of methane content increase the economic viability of the biomass gasification process. The criteria for the catalyst are fundamentally the same and can be summarized as follows [83]:

- The catalyst must be effective in the removal of tars.
- If the desired product is syngas, the catalyst must be capable of reforming methane.
- The catalyst should provide a suitable syngas ratio for the intended process.
- The catalyst should be inexpensive.
- The catalyst should be strong.
- The catalyst should be easily regenerated, and
- The catalyst should be resistant to deactivation.

Three main groups of catalysts include: (1) naturally occurring catalysts such as dolomite and olivine; (2) alkali metals such as KOH, K_2CO_3, $KHCO_3$, Na_2CO_3, $CaCO_3$, $CsCO_3$, KCl, $ZnCl_2$ and NaCl; and (3) nickel-based catalysts which have been evaluated for tar reduction in the syngas. The main catalysts for tar reforming are listed in Table 7 (adopted from [39]).

Table 5
The pyrolysis of different biomass for the production of hydrogen using different types of catalysts.

Biomass	Catalyst	Reactor type	Reaction temperature (°C)	Hydrogen yield	References
Oil palm shell	Ni	Fixed bed	900	37.28 vol.%	[55]
Oil palm shell	La/Al_2O_3	Fixed bed	900	38.45 vol.%	[55]
Saw dust	Cr_2O_3	Fixed bed	850	51.4 wt.%	[56]
Wood	Cu-Al-MCM-41	Fixed bed	500	9 vol.%	[57]
Olive husk	$ZuCl_2$	Tubular	700	70.3 vol.%	[54]
Cotton cocoon shell	$ZuCl_2$	Tubular	700	59.9 vol.%	[54]
Tea waste	$ZuCl_2$	Tubular	700	60.3 vol.%	[54]
Pine saw dust	Ni/Al	Fluidized bed	700	–	[58]
Rice straw	Cr_2O_3	Fixed bed	850	49.5 wt.%	[49]
Waste wood chips	ZSM-5 zeolite	Fluidized bed	550	0.08 wt.%	[59]

Table 6
The gasification of different biomass for the production of hydrogen using different types of catalyst (primary catalysts).

Biomass	Catalyst	Reactor type	Reaction temperature (°C)	Hydrogen yield	References
Almond shells	Olivine	Fluidized bed	770	52.2 vol.%	[64]
Spruce wood	Quartzite Olivine	Fluidized bed	780	31 vol.%	[67,68]
Cellulose	Rh/CeO_2	Fluidized bed	500–550	1290 μmol	[65]
Cellulose	$Rh/CeO_2/SiO_2$	Fluidized bed	600	38.66 vol.%	[69]
Cedar wood	$Rh/CeO_2/SiO_2$ (60)	Fluidized bed	550–700	1207 μmol	[70]
Apricot stones	Olivine Dolomite	Fixed bed	800	22.9 mol H_2/kg biomass	[71]
Legume straw Pine sawdust	Limestone Olivine Dolomite	Free-fall	750–850	43 mol%	[72]
Cedar wood Aspen	CaO	Tubular	850	29 cm^3/0.04 g bioma	[73]
Rice straw	Ni/olivine	Fluidized bed	800	31.5 vol.%	[74]
Wood	K_2CO_3	Fluidized bed	750	52.4 wt.%	[75]
GrapeOlive bagasse	$ZnCl_2$	Cylindrical	600	2.4 mol/kg biomass	[76]
Bagasse	$Ni–Al_2O_3$	Fixed bed	800	51.7 vol.%	[77]
Biomass	Fe, NiO	Tubular	950	119 g H_2/kg biomass	[78]
Biomass	Ni-based + calcium	Tubular	950	79.4 g H_2/kg biomass	[79]

Table 7
Main catalysts for tar reforming [39].

Catalyst type	Representative catalysts	Main advantages	Technical challenges
Maturely occurring catalyst	Dolomite Olivine Clay Zeolite	Cheap	Moderate reforming efficiency Easily eroded and broken
Alkali metals and salts	KOH $KHCO_3$ K_2CO_3 $NaCO_3$	1. Highly reforming efficiency 2. Increased hydrogen in syngas	Increased plugging and deactivation of other metal catalysts at a high temperature
Stable metal with oxide support	NiO/Al_2O_3 $Ni/CeO_2/Al_2O_3$	1. High reforming efficiency 2. Increased hydrogen in syngas	Stable metals are expensive Metals are easily deactivated by coke, poisoned by H_2S and sintered by ash melting Require hot-water-resistant support materials

Natural dolomite is the most popular catalyst used for tar elimination [41,84–89] since it is a cheap disposable catalyst that can significantly reduce the tar content of the syngas from a guard bed. The chemical composition, surface area and pore size of dolomite varies from source to source. Several studies using calcined dolomites, obtained by the decomposition of natural dolomite at high temperature >900 °C, as the secondary catalysts have shown great efficiency for tar removal from product gas [90]. For tar conversion it was demonstrated that the activity of dolomite increased with increasing Fe_2O_3 content in the catalyst and its pore size [85]. In another study, dolomite was mixed with Fe_2O_3 powder to increase its Fe_2O_3 content and it was observed that the addition of Fe_2O_3 led to slight increase in tar conversion at 850 °C [91]. While another research suggested that the presence of CaO in dolomite might be responsible for its activity in tar conversion [92].

Several research works published in the area of hot gas cleaning for biomass gasification use heterogeneous metal catalysts such as nickel and ruthenium, with support materials such as silica oxide and alumina oxide used to convert tar to gas [93–95]. Combinations of stable metals such as nickel or ruthenium and stable support materials such as zirconium and titanium have been developed for low-temperature steam reforming of tar [96]. Although nickel and other stable metal catalysts can almost completely remove tar, they are expensive, easily deactivated and poisoned at high temperature. Several groups [68,97–100] have investigated a system of raw gas cleaning that involves a combined of nickel–dolomite or alkali metal catalyst for steam reforming of tar using metallic nickel as

Table 8
The catalytic cracking of tar using different types of catalyst.

Biomass	Catalyst	Reactor type	Reaction temperature (°C)	Tar conversion (%)	References
Birch	Chinese dolomite	Fixed bed	750	68	[84]
Birch	Sala dolomite	Fixed bed	750	71	[84]
Wood	Norte dolomite	Fixed bed	875	95	[85]
Wood	Sevilla dolomite	Fixed bed	875	77	[85]
Wood	Malaga dolomite	Fixed bed	840	96	[86]
RDF	Limestone Dolomite	Fixed bed	800	–	[88]
Biomass	Dolomite	Fixed bed	910	98	[89]
Wood	Ni/dolomite + Fe_2O_3	Fixed bed	750	97	[91]
Wood	Ni/Al_2O_3	Fixed bed	900	100	[92]
Wood	Ni/dolomite	Fixed bed	800	97	[100]
Pine wood	Ni-based + dolomite	Fixed bed	830	98	[101]
Biomass	Ni/zeolite	Fixed bed	750	99	[102]
Birch	Metallic iron	Fixed bed	800	92	[103]
Wood	Nano-Ni-La-Fe/γ-Al_2O_3	Fixed bed	800	99	[104]

an active phase grafted on dolomite. Their results showed that 98% of tar removal was obtained at a reforming temperature of 750 °C with an increment in the hydrogen and carbon monoxide content and a reduction of the hydrocarbon and methane content from the outgoing gas. Furthermore, there was no obvious deactivation of catalyst observed in 60 h tests [91].

Dolomite or alkali catalyst for the removal of tar (up to 95%) and nickel-based catalyst for reforming of the methane and remaining tar are the most conventional and active catalysts. The majority of published work focus on commercially available nickel catalysts designed for steam reforming of hydrocarbons and methane and increasing hydrogen and carbon monoxide content. A summary of catalytic cracking researches is tabularized in Table 8.

9. Conclusions

Malaysia is currently the world's largest producer and exporter of palm oil. Besides producing palm oil, at present there is an increasing interest concerning oil palm renewable energy, and one of major attentions is the production of hydrogen from biomass by catalytic routes.

There are various thermo-chemical conversion technologies which can be applied for hydrogen production from biomass. Gasification technology provides a competitive way to convert solid biomass like oil palm waste to a uniform gas mixture namely hydrogen, carbon monoxide, methane and carbon dioxide. Catalysts are widely used for syngas cleaning and play an important role in enhancing the production of hydrogen by gasification process. Various catalytic systems have been studied to improve hydrogen production and reduce tar content in syngas produced from biomass. Calcined dolomite can be an effective catalyst for minimizing tar in the product gas. Dolomite activity can be directly related to the CaO content, Fe_2O_3 content, pore size and distribution. A major problem with using dolomite is the deactivation due to carbon deposition and it is a soft and fragile material; however, dolomite is cheap and can be easily replaced.

A significant amount of work has been published on the area of hot gas cleaning from biomass gasification using nickel catalysts. Nickel-based supported catalysts are highly effective at the removal of tar and adjustment of the gas composition to syngas quality. The additional of nickel to dolomite and olivine could significantly improve the activity towards tar conversion.

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